

Cell for bleaching and disinfecting and use of this cell in laundry washing machines

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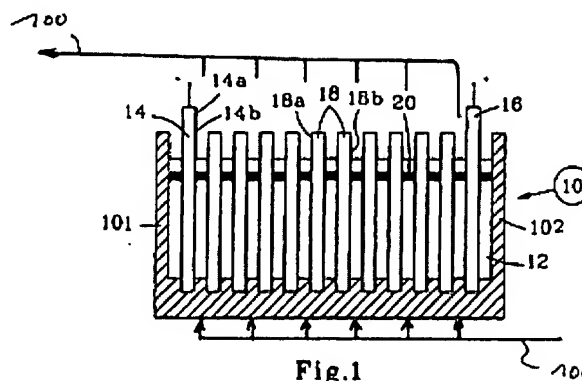
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 EP1031645
 US4203821
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Abstract of EP1036874

The whitening-disinfecting system is new. The cell comprises anode and cathode with at least one bipolar electrode placed between and consisting of substrate made of conductive material coated with compact layer of diamond made conductive by means of dopant (preferably boron). The thickness of diamond layer is preferably 0.1 - 1 micron. Bipolar electrode is preferably in form of plate or the cell may contain a number of bipolar electrodes in form of balls.



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<!--StartFragment-->Description of EP1036874 [0001] La présente invention concerne, de manière générale, une cellule de blanchiment et de désinfection et son application aux machines à laver le linge. Plus particulièrement, elle concerne une cellule d'électrolyse à électrode bipolaire (ou électrode bipolaire), c'est-à-dire une cellule dans laquelle l'anode et la cathode sont séparées par au moins une troisième électrode, dite électrode bipolaire, formant elle-même à la fois une anode et une cathode.

[0002] Une cellule d'électrolyse à électrode bipolaire particulièrement avantageuse pour traiter les eaux usées, parce qu'elle permet l'oxydation de leurs contaminants, a été décrite dans la demande de brevet français N0. 99 02 482. Il a été trouvé qu'une telle cellule permettait la génération d'ozone (O₃), en même temps que la production d'eau oxygénée (H₂O₂). Considérant la grande stabilité de l'électrode bipolaire et connaissant les propriétés de l'ozone et de l'eau oxygénée, il est donc proposé d'utiliser une telle cellule dans les machines à laver le linge, ou analogue, pour assurer, à la fois, une opération de désinfection et de blanchiment.

[0003] Les propriétés de l'ozone sont déjà connues. Il est également connu de générer de l'ozone par plasma ou par un appareillage à décharge électrique. Le coût et la complexité de tels appareils ne permettait pas d'envisager leur utilisation dans des machines à laver domestiques, ni même industrielles.

[0004] Le but principal de la présente invention est de proposer une cellule d'électrolyse à électrode bipolaire, présentant la double particularité d'avoir une longue durée de vie et de ne pas libérer de produit polluant dans l'électrolyte, et son application dans une machine à laver le linge pour assurer le blanchiment de ce dernier et sa désinfection.

[0005] De façon plus précise, la cellule d'électrolyse comporte une anode, une cathode et au moins une électrode bipolaire disposée entre l'anode et la cathode, et est caractérisée en ce que cette électrode bipolaire comporte un substrat en matériau conducteur et une couche compacte de diamant rendu conducteur par un dopant et recouvrant le substrat.

[0006] Avantageusement, l'anode et la cathode comportent également un substrat en matériau conducteur et une couche compacte de diamant rendu conducteur par un dopant et recouvrant le substrat.

[0007] Le matériau formant le substrat peut être choisi parmi le silicium et le carbure de silicium, tous deux rendus conducteurs par dopage. Il peut être aussi un métal réfractaire de transition choisi, de préférence, parmi le zirconium, le molybdène, le tantale, le niobium et le titane.

[0008] Selon une autre caractéristique de l'invention, le carbure de silicium se présente sous la forme d'un substrat poreux.

[0009] De préférence, le dopant utilisé pour rendre le diamant conducteur est du bore. La couche de diamant a, par ailleurs, une épaisseur de 0,1 à 1 µm.

[0010] La cellule utilisée selon l'invention peut comporter soit une électrode bipolaire sous la forme d'une plaque, soit une pluralité d'électrodes bipolaires sous la forme de billes.

[0011] D'autres caractéristiques de l'invention ressortiront de la description qui va suivre, faite en regard des dessins annexés, dans lesquels: la figure 1 représente une cellule d'électrolyse comportant des électrodes bipolaires formées de plaques, la figure 2 représente une cellule d'électrolyse comportant des électrodes bipolaires sous forme de billes en suspension, la figure 3 montre, en coupe, l'une des billes de la figure 2, et la figure 4 montre, en coupe, une variante de cellule d'électrolyse dont les électrodes bipolaires sont réalisées en carbure de silicium poreux.

[0012] Sur la figure 1, on peut voir, en coupe, une cellule d'électrolyse qui comporte un bac rectangulaire 10 en matériau isolant, contenant un électrolyte 12. Il comprend deux parois d'extrémité 101 et 102, au voisinage desquelles sont disposées respectivement une anode 14 et une cathode 16 se présentant sous la forme de plaques parallèles entre elles.

[0013] Plusieurs électrodes bipolaires 18, également formées de plaques, sont interposées, à intervalles réguliers, dans l'espace compris entre l'anode et la cathode, parallèlement à elles.

[0014] Bien entendu, l'anode 14, la cathode 16 et les électrodes bipolaires 18 ne doivent pas être en contact les uns avec les

Description of EP1036874 [0001] La présente invention concerne, de manière générale, une cellule de blanchiment et de désinfection et son application aux machines à laver le linge. Plus particulièrement, elle concerne une cellule d'électrolyse à électrode bipolaire (ou électrode bipolaire), c'est-à-dire une cellule dans laquelle l'anode et la cathode sont séparées par au moins une troisième électrode, dite électrode bipolaire, formant elle-même à la fois une anode et une cathode. [0002] Une cellule d'électrolyse à électrode bipolaire particulièrement avantageuse pour traiter les eaux usées, parce qu'elle permet l'oxydation de leurs contaminants, a été décrite dans la demande de brevet français N0. 99 02 482. Il a été trouvé qu'une telle cellule permettait la génération d'ozone (O₃), en même temps que la production d'eau oxygénée (H₂O₂). Considérant la grande stabilité de l'électrode bipolaire et connaissant les propriétés de l'ozone et de l'eau oxygénée, il est donc proposé d'utiliser une telle cellule dans les machines à laver le linge, ou analogue, pour assurer, à la fois, une opération de désinfection et de blanchiment. [0003] Les propriétés de l'ozone sont déjà connues. Il est également connu de générer de l'ozone par plasma ou par un appareillage à décharge électrique. Le coût et la complexité de tels appareils ne permettait pas d'envisager leur utilisation dans des machines à laver domestiques, ni même industrielles. [0004] Le but principal de la présente invention est de proposer une cellule d'électrolyse à électrode bipolaire, présentant la double particularité d'avoir une longue durée de vie et de ne pas libérer de produit polluant dans l'électrolyte, et son application dans une machine à laver le linge pour assurer le blanchiment de ce dernier et sa désinfection. [0005] De façon plus précise, la cellule d'électrolyse comporte une anode, une cathode et au moins une

Description of EP1036874 [0001] The present invention concerns, in a general way, a cell of bleaching and disinfection and its application to the washing machines. More particularly, it relates to a cell of electrolysis to bipolar electrode (or bipolar electrode), i.e. a cell in which the anode and cathode are separated by at least a third electrode, said bipolar electrode, forming itself at the same time an anode and a cathode. [0002] A cell of electrolysis to particularly advantageous bipolar electrode to treat used water, because it allows the oxidation of their contaminants, was described in the French patent application N0. 99 02.482. It was found that such a cell allowed the generation of ozone (O₃), at the same time as the production of hydrogen peroxide (H₂O₂). Considering the great stability of the bipolar electrode and knowing the properties of ozone and hydrogen peroxide, it is thus proposed to use such a cell in the washing machines, or analogue, to ensure, at the same time, an operation of disinfection and bleaching. [0003] The properties of ozone are already known. It is also known to generate ozone by plasma or an equipment with electric discharge. The cost and the complexity of such apparatuses did not make it possible to plan their use in washing machines domestic, nor even industrial. [0004] The principal goal of this invention is to propose a cell of electrolysis to bipolar electrode, having the double effect of having a long lifespan and of not releasing from product polluting in the electrolyte, and its application in a washing machine to ensure the bleaching of this last and its disinfection. [0005] In a more precise way, the cell of electrolysis comprises an anode, a cathode and at least a bipolar electrode laid out between the anode and cathode, and is characterized in that this bipolar electrode comprises a conducting material substrate and a compact layer of diamond made conducting by a doping agent and covering the substrate. [0006] Advantageously, the anode and cathode also comprise a conducting material substrate and a compact layer of diamond made conducting by a doping agent and covering the substrate.

[0007] The material forming the substrate can be selected among the silicon and the carbide of silicon, both made conducting by doping. It can be also a refractory metal of transition chosen, preferably, among zirconium, molybdenum, tantalum, niobium and titanium. [0008] According to another characteristic of the invention, the silicon carbide is appeared as a porous substrate. [0009] Preferably, doping it used to make diamond conducting is boron. The layer of diamond has, in addition, a thickness from 0,1 to 1 driven Mr.

[0010] The cell used according to the invention can comprise either a bipolar electrode in the shape of a plate, or a plurality of bipolar electrodes in the shape of balls. [0011] Other characteristics of the invention will arise from the description which will follow, made compared to the annexed drawings, in which: figure 1 represents a cell of electrolysis comprising of the formed bipolar electrodes of plates, figure 2 represents a cell of electrolysis comprising of the bipolar electrodes in the form of balls in suspension, figure 3 shows, out of cut, one of the balls of figure 2, and figure 4 shows, out of cut, an alternative of cell of electrolysis whose bipolar electrodes are made out of porous silicon carbide. [0012] On figure 1, one can see, out of cut, a cell of electrolysis which comprises a rectangular vat 10 out of insulating material, containing an electrolyte 12. It includes/understands two walls of end 101 and 102, in the vicinity of which an anode 14 and one cathode 16 are laid out respectively appearing itself as parallel plates between them. [0013] Several bipolar electrodes 18, also formed of plates, are interposed, with regular intervals, in the space ranging between the anode and cathode, parallel to them. [0014] Of course, the bipolar anode 14, cathode 16 and electrodes 18 should not be in contact the ones with the others. Holds 20 out of insulating material are thus interposed between them to this end. [0015] In the case of the use of such a cell of electrolysis in a washing machine, vat 10 is crossed by the liquid of washing according to flow's represented by arrows 100. It will be,

however, preferable to make cross the cell by the liquid only once the cycle of finished washing, which can be carried out by any known means of the expert such as, for example, of the valves ordered by the program of the washing machine. [0016] As well the anode 14 and cathode 16 as the bipolar electrodes 18 are made of a substrate electrically conducting, carrying the reference, covered on its two faces, at least in its immersed part, of a layer B of diamond doped to be electrically conductive. [0017] The substrate can be made of a plate of silicon or silicon carbide which, both, were doped, by known processes of the specialist of the profession, so as to reduce their resistivity to a value which, typically, is about 1 to 3 mΩ cm. The substrate can also be made of vitreous carbon or a composite material comprising a carbon fibre network amalgamated with carbon pyrolytic and/or silicon carbide. [0018] The substrate can be also a plate of metal, preferably a metal refractory of transition, advantageously selected among zirconium, molybdenum, tantalum, niobium or titanium. [0019] Whatever it is, the conducting substrate must initially carry diamond particles forming the germs of growth for the layer of diamond which is formed on its surface, according to a known process, by HFCVD (hot filament chemical vapor deposition) in an enclosure at a temperature ranging between 600 and 900 DEGREE C. diamond is made conducting by doping using boron which is introduced during the operation of deposit of the layer in the gas triméthylborane shape (TMB) or of any other substance (nitrogen, phosphorus, carbon) having the same effect. [0020] The process described above makes it possible to carry out anodes, cathodes and bipolar electrodes covered on their two faces with a diamond film to compact polycrystalline structure, whose resistivity is lower or equal to 0,2 Ω cm, for a boron concentration of 3500 ppm approximately. The thickness of this conducting layer of doped diamond, typically, lies between 0,1 and 1 μm. [0021] For more details on manufacture of such electrodes, one will refer to the article entitled "Diamond electrodes

and microelectrodes" of A. Perret and Al, published in Electrochemical Society Proceedings, Volume 97-32. [0022] In alternative, the external faces of the anode 14 and cathode 16 (i.e. those which are compared to ends 101 and 102 of the vat) can be also covered with a layer of diamond. [0023] According to another alternative, only the bipolar electrodes are produced as indicated above, the anode and cathode being then in a conducting material, such as silicon, carbide of silicon, graphite, vitreous carbon, a composite material containing carbon fibres, as mentioned previously, or of tantalum, titanium, zirconium, niobium or molybdenum. [0024] Figure 2 shows another type of cell of electrolysis using of the bipolar electrodes in the form of balls. This cell comprises a cylindrical vat 22 inside containing a tubular anode 24 and one cathode in the shape of stem 26 laid out according to the axis of the anode. The anode 24 and cathode 26, are put besides their form, and thus concerning the substrate and the layer of diamond which constitute them, identical to the electrodes 14 and 16 described in the mode of realization of figure 1. [0025] The vat 22 comprises, at its base, an entry 22a and, with its higher part, an exit 22b, respectively intended to make penetrate and leave a solution electrolyte 28. A membrane 30 is placed in the lower part of the vat, under the two electrodes and above the entry 22a. It has a porous structure, so as to let pass the electrolyte when it goes up entry 22a towards the exit 22b. Bipolar electrodes 32, formed of a plurality of spherical particles maintained in suspension in the electrolyte are laid out in the space located above the membrane. Their diameter, typically, lies between 0,5 and 10 Micrometers the structure of the membrane is selected so that these balls cannot cross it. [0026] As shown in the figure 3, each bipolar electrode 32 comprises a spherical core 34, advantageously out of doped silicon carbide, by known processes of the specialist of the profession, in order to reduce its resistivity to a value of about 1 to 3 mΩ cm. The ball thus made conducting is completely covered with a layer 36 of conducting diamond doped

with boron having, typically, a thickness of about 0,1 to 1 driven Mr. As indicated in connection with the realization of the electrodes of figure 1, doping with boron is carried out using gas triméthylebore (TMB) introduced into enclosure HFCVD lasting the operation of deposit of diamond. As already mentioned, other doping agents, such as the nitrogen, phosphorus or carbon, can be used to make electrically diamond conducting. This layer has a compact polycrystalline structure, so that core 34 is completely protected. [0027] The manufacture of covered diamond silicon carbide balls is known for applications in ball bearings. For more details, one will refer, for example, with the publication of Mr. Drory and Microstructural Al entitled << effects on the performance of CVD diamond coatings for bearing applications >> to the 2nd International Conference on the Applications of Diamond Films and Related Materials >>, held in Tokyo in 1993. [0028] Spherical bipolar electrodes thus obtained make it possible to avoid a wear and a pollution, only fact that they are covered with a layer of diamond. [0029] The doped silicon carbide is selected to constitute the core of the bipolar electrodes, because of its low density which makes it possible these balls 32 to remain in suspension in the electrolyte when this one goes up in the vat. In alternative, core 34 of the spheres can however be out of doped silicon, graphite or refractory metal of transition and, more particularly, zirconium, molybdenum, tantalum, niobium or titanium. [0030] Figure 4 presents an alternative of cell advantageously being able to be used according to the invention. According to this alternative, the bipolar electrodes 130, the anode (+) and cathode (-) are made out of porous silicon carbide which, after doping with boron, is then covered with a layer of diamond according to processes' indicated above. It follows that the structure of the electrodes allows the passage of the liquid in a transverse way, as indicated by arrows 110 and 120. From the larger effective surface of the electrodes and the provision of flow, the effectiveness of

such a cell is improved and its
facilitated assembly. It is still
advisable to note that ozone (O3) is
generated side of the anode, while
hydrogen (H2) is generated side of
cathode. -----

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